

U.S. Serial No. 10/652,390
Reply to Office Action of: 11/30/06
Family Number: P2002J085 US2

Page 12

Remarks

The present invention is directed to an unsulfided hydrodewaxing catalyst comprising a Group VIII metal component and a dewaxing component wherein said catalyst is made by reduction followed by treatment at a temperature below hydrodewaxing temperatures with a hydrocarbon stream containing one or more oxygenates in an amount of at least 100 ppm, measured as oxygen, and wherein said Group VIII metal is Pt, Pd or mixtures thereof.

It is also directed to a process for hydrodewaxing waxy Fischer-Tropsch hydrocarbons produced over a non-cobalt catalyst to produce a dewaxed base stock, the process comprising contacting the waxy Fischer-Tropsch hydrocarbons with hydrogen in the presence of the aforementioned catalyst.

The Examiner rejects claims 1-12 under 35 USC § 103(a) as obvious over Duprey et al. (WO 01/07538) in view of Borghard et al. (WO 96/03359).

The Examiner argues that Duprey discloses a catalyst composition comprising a hydrogenation component, a surface dealuminated aluminosilicate zeolite crystallite and a low acidity refractory oxide binder material which is essentially free of alumina. Suitable alumino-silicates include mordenite, Beta, ferrierite, ZSM-11, ZSM-5, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48, ZSM-57, SSZ-23, SSZ-24, SSZ-25, SSZ-26, SSZ-32, SSZ-33, MCM-22 and mixtures thereof. The hydrogenation component can be at least one of Group VIB, and/or Group VIII.

The Examiner acknowledges that Duprey does not disclose treatment of the dewaxing catalyst with a stream containing one or more oxygenates or the details of FT catalysts or synthesis process or the use of an alumina binder for the dewaxing catalyst.

U.S. Serial No. 10/652,390
Reply to Office Action of: 11/30/06
Family Number: P2002J085 US2

Page 13

The Examiner cites Borghard as disclosing zeolite B modified with boron, tin, lead or indium and combined with a hydrogenation/dehydrogenation component to convert FT heavy ends which contain paraffins, olefins and oxygenates into low pour point distillates with high cetane number and extra high VI lube oil. The lube oil can then be dewaxed using conventional solvent dewaxing processes or catalytic dewaxing processes or by increasing the severity of the hydroisomerization step. If the catalyst is to be steamed in order to achieve low acidity the steaming is performed after the catalyst has been formulated with the binder. Steaming typically utilizes a 100% steam atmosphere at 430-590°C for 12-48 hours.

Borghard discloses the FT process and FT catalysts.

The Examiner concludes that it would have been obvious to one skilled in the art at the time the invention was made to combine Duprey and Borghard and treat the catalyst with steam to reduce its acidity and make it more useful for dewaxing, to use the FT catalyst of Borghard in Duprey because both use FT product for hydrodewaxing and to use the alumina binder of Borghard in Duprey.

Applicants respectfully traverse this rejection.

In Duprey, the Fischer-Tropsch wax feed is described as not containing sulfur, nitrogen or metal impurities normally found in crude oil BUT it is known to contain water, trace metals and a number of unsaturated compounds and oxygenate compounds such as alcohols, ketones, aldehydes etc. which compounds "may cause a deactivation of certain catalysts used in further downstream treatment of the Fischer-Tropsch product" [page 3, lines 32-34].

U.S. Serial No. 10/652,390
Reply to Office Action of: 11/30/06
Family Number: P2002J085 US2

Page 14

Consequently, the Fischer-Tropsch wax feed is subjected to a hydrotreatment process step in order to lower the content of these unsaturated or oxygenated products. While in Example 4 it is recited that the F-T wax has been subjected to hydrotreatment in order to reduce the oxygen content to below 500 ppmw as molecular oxygen, this cannot be taken as a statement that any molecular oxygen actually remained in the thus treated FT wax. Consequently, it cannot be said that the catalyst used in Example 4 (the catalyst of Example 3) ever actually came into contact with a FT wax stream containing any molecular oxygen and further it cannot be said that the benefit associated with exposing a reduced hydrodewaxing catalyst to oxygenates, as taught in the present application, ever was actually secured in the prior art. "Below 500 ppmw" includes zero as well as 499 ppmw, with no clear actual value being taught. No clear teaching is presented as to just how far "below" 500 ppmw or "above" zero ppmw the molecular oxygen content of the FT was reduced or adjusted.

The reference does not teach, suggest or imply the beneficial result secured when the hydrodewaxing catalyst is deliberately exposed to oxygenates subsequent to the reduction of the catalyst in hydrogen but prior to the use of the catalyst for hydrodewaxing.

The reference is very clear in its teaching that it is desirable, if not indeed also necessary, in order to avoid catalyst deactivation, to hydrotreat the FT wax feed to remove olefins and oxygenates prior to any hydroisomerization. This cannot be taken as teaching, suggesting or implying that a hydrodewaxing catalyst actually be deliberately treated with oxygenates prior to being used for hydrodewaxing, nor as teaching, suggesting or implying that subjecting a reduced catalyst to an oxygenate treatment would or could result in an improvement in the catalyst selectivity for hydroisomerization and a reduction in the gas make during hydrodewaxing.

U.S. Serial No. 10/652,390
Reply to Office Action of: 11/30/06
Family Number: P2002J085 US2

Page 15

The reference never recites that the FT wax feed must contain at least one oxygenate in an amount of less than 500 ppmw, but rather that the FT wax feed is hydrotreated to reduce its oxygenate content to "below 500 ppmw" as molecular oxygen. The presence of oxygen is never positively recited, all this is taught or suggested in that it is highly desirable that the oxygenates be removed from the feed prior to hydroisomerization.

This teaching of Duprey, that it is highly desirable that oxygenates be removed from the feed prior to hydroisomerization over a catalyst comprising a hydrogenation-dehydrogenation metal component on a surface dealuminated aluminosilicate zeolite, must be kept in mind as a teaching of the state of the art when considering Borghard. Duprey is a warning that the hydroisomerization feed be deoxygenated prior to being hydroisomerized.

Borghard teaches a process for treating FT hydrocarbon feedstocks over a zeolite Beta catalyst modified with boron, tin, lead or indium, combined with a hydrogenation/dehydrogenation component. In Borghard the zeolite Beta with, e.g. boron in the framework is composited with a matrix material to form a finished catalyst. The matrix material is non acidic, such as alumina, silica-alumina or silica. The zeolite Beta/matrix mixture is formed by, e.g. mulling the individual components followed by extrusion of pellets.

While Borghard at page 8 lines 3-6 recite that

"If the catalyst is to be steamed in order to achieve the desired low acidity, it is performed after the catalyst has been formulated with the binder, as is conventional."

it is clear that Borghard makes no mention of any reduction step in the forming of the catalyst. While steaming can be done before or after compositing, it is not taught in Borghard that a reduction step constitutes part of any catalysts preparation process.

U.S. Serial No. 10/652,390
Reply to Office Action of: 11/30/06
Family Number: P2002J085 US2

Page 16

Indeed, in Borghard no statement or teaching of any kind is given or made regarding the practice of a reduction step in catalyst preparation.

Borghard produces catalyst by producing a modified zeolite Beta (e.g., boron modification) followed by compositing the modified zeolite Beta with a binder (e.g., silica) which mixture is extruded, dried and calcined (i.e., heated or burned in air or oxygen). The calcined extrudate is then exchanged with ammonium nitrite solution after which it is again calcined. The calcined material (called the exchanged catalyst) is then steamed.

Following steaming the catalyst is finally loaded with a catalytically active metal (in this case platinum in the form of platinum tetraamine chloride) followed by a calcinations step. At no point is "reduction" mentioned, taught or even suggested.

As is clear, the steaming which may be conducted after catalyst formation is a steaming step conducted after the modified zeolite Beta has been composited with the binder.

Nothing in Borghard teaches, suggests or implies that a steaming step can or should ever be performed following a catalytically active metal loading step.

Bearing in mind the teaching of Duprey that any oxygenates present in a hydrocarbon feed must be reduced prior to any hydroisomerization step, it is readily apparent that one skilled in the art would be demotivated to steam a fully formed catalyst, one composing a catalytically active metal component on a zeolite in combination with a binder, which finished catalyst has been reduced to prepare it for use.

Duprey teaches away from exposing such a catalyst to any oxygenates.

U.S. Serial No. 10/652,390
Reply to Office Action of: 11/30/06
Family Number: P2002J085 US2

Page 17

The Examiner rejects claims 14-26, and 30-63 under 35 USC § 103(a) as obvious over Duprey et al in view of Borghard et al.

The Examiner argues that Duprey teaches a process which yields base oil products having high VI and low pour point by contacting a synthetic wax such as FT wax, which has not been subjected to a hydroisomerization treatment, with a catalyst composition comprising at least one hydrogenation component, a dealuminated aluminosilicate zeolite and a binder essentially free of alumina. The FT wax does not contain sulfur, nitrogen or metal impurities normally found in crude oil but is known to contain water, trace metals, and a number of unsaturated compounds and oxygenates such as alcohols, ketones, aldehydes, etc.

Applicants respectfully traverse this rejection.

Duprey teaches a process for preparing a lubricating base oil by contacting a synthetic wax such as FT wax, which has not been hydroisomerized, with a catalyst comprising at least a hydrogenation component, dealuminated aluminosilicate zeolite and a low acidity refractory metal oxide binder essentially free of alumina.

As taught by Duprey, the FT wax is known to contain water, trace metals and unsaturated compounds and oxygenates. Duprey also expressly teaches that oxygenates "may cause deactivation of certain catalyst used in further downstream treatment of the Fischer-Tropsch product" [see page 3, lines 32-34].

As a consequence to this presence of oxygenation in the FT wax in Duprey the FT wax is subjected to hydrotreatment in order to reduce the oxygenate content. In Example 4 the oxygenate content is reduced to "below 500 ppmw" as molecular oxygen. As previously argued above, "below 500 ppmw" cannot be taken as

U.S. Serial No. 10/652,390

Reply to Office Action of: 11/30/06

Family Number: P2002J085 US2

Page 18

a recitation that any oxygenates actually remained in the hydrotreated FT wax feed. "Below 500 ppmw oxygenates" embraces zero as well as 499 ppmw. No clear or unambiguous oxygenates content level is recited. What is positively recited, however, is the clear teaching that the presence of oxygenates in the FT wax feed is not desirable and that ways must be practiced to remove the oxygenates from such FT wax feed so as to avoid deactivation of certain catalysts used in further down stream treatment of the FT wax.

No benefit is associated with retaining oxygenates in the FT wax feed. All that is clearly taught is that the presence of oxygenates in FT wax feed is detrimental!

Consequently Duprey cannot be taken as teaching, suggesting, implying or motivating any practitioner skilled in the art of catalytic hydroisomerization to deliberately treat the hydroisomerization catalyst, following reduction, with a hydrocarbon feed containing oxygenates at any temperature, including temperatures below the hydroisomerization process temperature, prior to being employed in the hydroisomerization process.

Borghard does not rectify this defect.

Nothing in Borghard teaches, suggests, implies or acts to motivate one skilled in the art to contact a reduced catalyst with a hydrocarbon feed containing oxygenates prior to being used catalytically in a hydroisomerization process.

Borghard teaches steaming of a modified zeolite Beta catalyst material following it being composited with a binder. This is not a finished catalyst but only a mixture of zeolite Beta and binder. There has been no reduction step. Indeed, in

U.S. Serial No. 10/652,390
Reply to Office Action of: 11/30/06
Family Number: P2002J085 US2

Page 19

Borghard only calcinations steps are recited, even after catalytic metal has been added to the steam zeolite Beta/binder combination.

Borghard does not teach, suggest, imply or motivate one skilled in the art to treat a finished, reduced catalyst with a hydrocarbon stream containing one or more oxygenates in an amount of at least 100 wppm measured as oxygen, such treatment to be conducted at a temperature below hydrodewaxing temperatures.

Borghard cannot be read in a vacuum. Borghard, which steams its unreduced but calcined zeolite Beta/binder composite prior to the addition of any metal cannot be seen as suggesting that Duprey be modified to include a step of subjecting a reduced metal containing catalyst to a treatment with a hydrocarbon fluid containing oxygenates at 100 wppm, as molecular oxygen, when Duprey itself teaches that oxygenates are detrimental to isomerization catalysts and are to be removed from the feed by hydrotreatment before the feed is subjected to isomerization over the catalyst.

It is believed the present invention is not obvious over this combination of references.

As demonstrated in the present application, treatment of the reduced catalyst with a hydrocarbon feed containing oxygenates prior to using the catalyst for hydroisomerization resulted in a process which had a lower gas make than did a process using a reduced catalyst which had not been so treated (See paragraph 0046 and Figure 2). Further, the yield of dewaxed oil for a given pour point was higher in the process using the reduced catalyst which had been pretreated with the oxygenate containing hydrocarbon stream as compared to the process using the reduced catalyst in the untreated form (Paragraph [0047] and Figure 3). This is totally unexpected in view of Duprey which argues and teaches that oxygenates are detrimental and need to be

U.S. Serial No. 10/652,390
Reply to Office Action of: 11/30/06
Family Number: P2002J085 US2

Page 20

removed from the feed prior to hydroisomerization to avoid deactivation of such catalyst.

It has been unexpectedly discovered that pretreating a reduced catalyst with an oxygenate containing stream prior to practicing hydrodewaxing is as effective as sulfiding such a catalyst in terms of gas make and dewaxed oil product yield. Unexpectedly, the oxygenate treatment doesn't deactivate the catalyst as one would have expected from the teachings of Duprey, but rather reduces gas make and increases yield for a given pour point as compared to the untreated catalyst.

The Examiner rejects claim 27 under 35 USC § 103(a) as obvious over Duprey in view of Borghard and further in view of Ziemer (USP 4,867,862).

Ziemer is cited as disclosing a single stage, multi-layered catalyst system for hydrodehazing and hydrofinishing a hydrocracked, solvent dewaxed lube oil base stock.

The Examiner argues that it would have been obvious to combine Duprey, Borghard and Ziemer and dehaze the stock for a better quality lubricant.

Applicants respectfully traverse this rejection.

Applicants have demonstrated why Duprey and Borghard cannot be seen as rendering the present invention obvious. Duprey teaches against the presence of oxygenates in feed sent to an isomerization unit, arguing that oxygenates in FT wax feed are detrimental to catalysts used to treat FT wax downstream, i.e., in a hydroisomerization or hydrodewaxing step. Duprey teaches that oxygenates in FT wax feed will probably deactivate such catalysts.

U.S. Serial No. 10/652,390
Reply to Office Action of: 11/30/06
Family Number: P2002J085 US2

Page 21

Borghard subjects a calcined zeolite beta/binder composite to steam, then adds catalytic metal and calcines again to produce its catalyst. Borghard cannot be seen as teaching, suggesting, implying or motivating one skilled in the art to subject a reduced metal catalyst to treatment with an oxygenate containing hydrocarbon stream, for to do so contradicts the very teaching of Duprey.

Because the two primary references, Duprey and Borghard, fail the teaching of Ziemer is irrelevant and claim 27 dependent ultimately on independent claim 14 shown to be patentable over Duprey and Borghard must similarly be patentable.

The Examiner rejects claims 29 and 64 under 35 USC §103(a) as obvious over Duprey in view of Borghard and further in view of Derr, Jr., et al (USP 4,684,756).

The Examiner argues that while Duprey and Borghard do not mention non-shifting FT catalysts, Derr, Jr. addresses conversion of low H₂/CO ratio syngas wherein it is essential that the CO reducing catalyst used include water-gas shift activity so that steam formed in the FT operation will react with charged CO to form H₂.

The Examiner concludes that because Duprey and Borghard do not mention shift activity, it would have been obvious to use a non-shift catalyst because the shift reaction is not intended by the present applicants to be in their invention because the present applicants are treating the FT products in a dewaxing operation.

Applicants respectfully traverse this rejection.

As previously indicated Duprey and Borghard are ineffective to make the underlying process of the present applicants obvious. Because the two primary references are ineffective in rendering obvious the hydrodewaxing of FT waxy

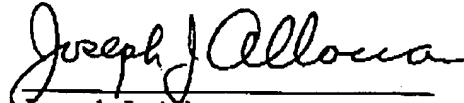
U.S. Serial No. 10/652,390
Reply to Office Action of: 11/30/06
Family Number: P2002J085 US2

Page 22

hydrocarbons over a reduced catalyst which reduced catalyst is treated with a hydrocarbon stream containing at least 100 wppm oxygenates as oxygen at temperatures below the hydrodewaxing temperature, the teaching of Derr, Jr. et al. regarding the FT wax synthesis process is irrelevant, and claims 29 and 64 are patentable.

It is requested that the Examiner reconsider the present application in light of the arguments presented above, that he withdraw the rejections, allow the claims and pass the case to issue in due course.

Respectfully submitted,



Joseph J. Allocca

Attorney for Applicant(s)

Registration No. 27,766

Telephone Number: (908) 730-3629

Facsimile Number: (908) 730-3649

☒ Pursuant to 37 CFR 1.34(a)

ExxonMobil Research and Engineering Company
P. O. Box 900
Annandale, New Jersey 08801-0900

JJA:jdw
2/12/07